

MICROFILTRATION NZP CERAMIC BASED ON NETWORK ALKALINE-EARTH PHOSPHATES

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A solar furnace based technology for high-temperature synthesis of NZP structure was implemented. X-ray phase analysis was used to study phase-formation in the systems obtained. It was determined that the Ca, Sr, and Ba phosphates obtained by melting belong to an NZP-type structural group. It was shown experimentally that strong porous monophase NZP ceramics can be obtained by conventional sintering.

Key words: NZP structure, solar furnace, high-temperature synthesis, melting, x-ray phase method, phosphates, alkaline-earth metals, microfiltration, porous ceramic.

The continually increasing demand for new ceramic materials obtained by modern technologies has made it necessary to investigate compound such as orthophosphates which have a network structure and crystallize in the $\text{NaZr}_2(\text{PO}_4)_3$ structure (NZP structure).

The interest in NZP phosphates is explained by the prospects of using them as high-tech ceramic materials which undergo practically no expansion when heated and possess chemical and thermal stability, hardness, strength, high ionic conductivity, catalytic activity, high melting temperature, and low thermal conductivity [1].

A characteristic of this structure is its ability to realize wide fields of iso- and heterovalent isomorphism with the participation of a large number of chemical elements in Mendeleev's periodic chart. The possibility of including different metals in a stable structure with low solubility is one of the important virtues of network-structure phosphates for creating diverse monophase functional ceramics based on them [2].

At the same time the published data on the crystal structure of these compounds are contradictory and the processes resulting in the formation of such compounds during synthesis by different methods in order to obtain bulk samples have been little studied.

Several methods of synthesizing compounds with NZP structure are known: the ceramic method, heating hydrogels or xerogels, and hydrothermal synthesis. The formation process for such compounds is complex, which makes it difficult to choose the method and conditions of synthesis for obtaining a pure phase of the expected products [3, 4].

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The sol-gel method, which is most often used to obtain network phosphates, is characterized by poor reproducibility and results in systems with three-dimensional nonuniformity of the distribution of the components which requires additional processing (grinding) of the powders. High annealing temperatures are required to obtain crystalline systems by this method. Hydrothermal processing of sols makes it possible to obtain only some crystalline NZP phosphates. For this reason, the problem of advancing the existing methods of synthesis and developing new ones so as to obtain systems with the required properties is still topical.

In this work, network zirconium phosphates of the alkaline-earths Ca, Sr, and Ba were synthesized by melting mixtures in optical furnaces [5]. The phase composition and the porous structure of the ceramic obtained were studied in detail by physical-chemical methods at each stage of the technological process. This made it possible to determine the parameters required for the synthesis of such systems as well as for obtaining ceramic porous samples.

The aim of the present work was to investigate the effectiveness of synthesizing the NZP-structure of $\text{MZr}_4(\text{PO}_4)_6$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) as a function of the conditions of thermal action in an oxidizing medium. The temperature range for these studies was from 200°C to the melting point of the mix. A comparative analysis of the ceramic sintering of NZP compounds obtained by solid-phase synthesis and melting of the mix was performed.

The initial compositions for obtaining ceramic samples correspond to the stoichiometric composition of NZP compounds.

A powder mixture of an alkaline-earth oxide or the corresponding hydroxides or carbonate salts (CaO , $\text{Ca}(\text{OH})_2$, CaCO_3 , BaCO_3 , $\text{Ba}(\text{OH})_2$, SrCO_3 , $\text{Sr}(\text{OH})_2$), zirconium in form of the oxide ZrO_2 , and a phosphate in the form of am-

TABLE 1. Crystallographic Data on Compounds with NZP Structure Based on Alkaline-Earth Elements

Phosphates	Heat-treatment	NZP structure present	Lattice parameter, Å	
			<i>a</i>	<i>c</i>
$\text{CaZr}_4(\text{PO}_4)_6$	1200°C	Traces of NZP structure	—	—
	Melting in solar furnace*	Single-phase $\text{CaZr}_4(\text{PO}_4)_6$	8.7832 ± 0.0022	22.6415 ± 0.010
$\text{SrZr}_4(\text{PO}_4)_6$	1200°C	Single-phase $\text{SrZr}_4(\text{PO}_4)_6$	8.6765 ± 0.002	23.3706 ± 0.002
	Melting in solar furnace*	Single-phase $\text{SrZr}_4(\text{PO}_4)_6$	8.6765 ± 0.002	23.3706 ± 0.002
$\text{BaZr}_4(\text{PO}_4)_6$	1200°C	Absent	—	—
	Melting in solar furnace*	Single-phase $\text{BaZr}_4(\text{PO}_4)_6$	8.6533 ± 0.002	24.0467 ± 0.002

* Melting temperature about 1800°C [1]. Heat flux density in the melt zone 400 – 600 W/cm².

monium salts $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$ was used. The homogenized mix was dried in air and heated at 200 – 900°C to remove gaseous reaction products (CO_2 , NH_3 , H_2O).

The powder material processed in this manner was pressed into pellets under pressure 30 – 60 MPa and kilned by means of two technologies:

- solid-phase synthesis in the temperature regime 1000 – 1200°C (soaking in resistance furnaces for 24 – 40 h);
- high-temperature heating to the melting state in a solar furnace (SF) (soaking time 1 – 7 min); compounds with the molecular formula $\text{M}\text{Zr}_4(\text{PO}_4)_6$ were synthesized at heat flux density 400 – 600 W/cm².

The heat-treated material was investigated by x-ray phase analysis using a DRON-2 diffractometer with CuK_α filtered radiation, $\lambda_{\text{Cu}} = 1.54078$ Å (Table 1). The lattice parameters were calculated for a single-phase NZP structure according to the diffraction peaks *hkl* 300 and 116.

The investigations showed that for solid-phase synthesis of NZP compounds based on alkaline-earth elements Ca and Ba even long soaking times 25 – 40 h at 1200°C are inadequate and do not secure complete synthesis. This can cause ceramic articles to crack during final sintering.

At the same time the x-ray diffraction patterns of all compounds based on alkaline-earth metals obtained by melt-

ing in solar furnaces show that the compounds crystallize in an NZP type structure (see Fig. 1).

To obtain massive porous ceramic samples the synthesized material was subjected to wet grinding in a planetary mill with zirconium balls. The mass ratio (powder : grinding balls : water) was 1 : 3 : 1. Grinding was continued for 10 h. The grinding time was adjusted depending on the fraction composition required for the material ($\ll 50$ µm). The balls

TABLE 2. Characteristics of Shrinkage Phenomena Occurring during Sintering of Ceramic Samples Based on NZP Compounds

Initial components	Initial powder heat-treatment regime	Ceramic sintering temperature, °C	Shrinkage, %*
CaCO_3	1200°C, 24 h	1000	+2.00
ZrO_2		1200	+2.73
$(\text{NH}_4)_2\text{HPO}_4$		1250	+4.67
		1300	+5.00
	Melting in solar furnace**	1000	0.00
		1200	0.00
		1215	-0.66
		1250	-4.50
		1300	-5.40
		1350	-12.00
SrCO_3	1200°C, 24 h	1220	-0.70
ZrO_2		1300	-5.35
$(\text{NH}_4)_2\text{HPO}_4$		1350	-7.60
	Melting in solar furnace**	1300	-4.20
		1450	-5.00
BaCO_3	1200°C, 24 h	1220	+0.44
ZrO_2		1350	+1.67
$(\text{NH}_4)_2\text{HPO}_4$		1450	+2.23
	Melting in solar furnace**	1300	-2.29
		1430	-3.31
		1550	-9.93

* "+" and "-" — increase and decrease of the sample size.

** The melting temperature is about 1800°C [1]. The heat-flux density in the melt zone is 400 – 600 W/cm².

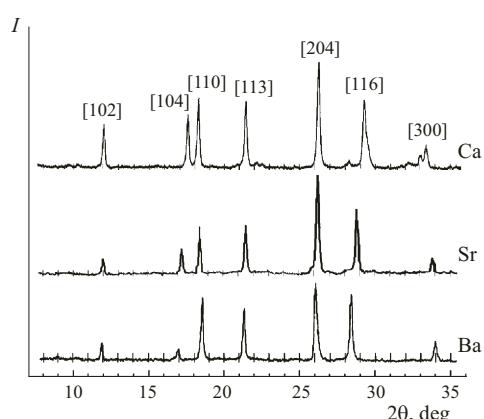


Fig. 1. X-ray diffraction pattern of orthophosphates with NZP structure synthesized by melting in optical furnaces (solar furnaces): Ca $\text{CaZr}_4(\text{PO}_4)_6$; Sr $\text{SrZr}_4(\text{PO}_4)_6$; Ba $\text{BaZr}_4(\text{PO}_4)_6$.

TABLE 3. Properties of Porous Ceramic Samples Based on Alkaline-Earth NZP Structure Synthesized in Solar Furnaces

Phosphates	Production technology		Ceramic properties						
	Content of process additives, wt.%	Kilning temperature, °C	Shrinkage, %	σ_c , MPa	P, %	ρ , g/cm ³	d_{\max} , μm	d_{\min} , μm	K , μm ²
CaZr ₄ (PO ₄) ₆	—	1250	-4.50	—	—	—	—	—	—
	—	1300	-5.46	24.3	29.44	2.432	9.0	4.5	0.06
	20 coke	1300	-7.00	72.0	46.50	1.762	18.3	11.5	2.27
	—	1350	-12.00	84.4	21.86	2.680	—	—	—
SrZr ₄ (PO ₄) ₆	—	1300	-4.20	50.6	33.44	2.226	—	—	—
	—	1430	-5.00	—	—	—	6.2	2.9	0.07
BaZr ₄ (PO ₄) ₆	0.5 MgO	1300	-2.20	30.7	37.96	2.196	10.4	2.4	0.06
	0.5 MgO	1430	-3.31	—	—	—	—	—	—
	0.5 MgO	1550	-9.93	—	21.34	2.68	—	—	—

were separated from the liquid mixture, which was dried at 110°C to a dry powder.

The initial ceramic mix includes a disperse NZP-compound powder and a binder based on 3% solution of carbo-methylcellulose. Only samples based on a polydisperse filler were studied. The powders were not separated into fractions. Comminution of the material obtained does not present any difficulties to 20 – 50 μm. The additions for sintering (MgO) were introduced for samples based on barium.

The properties were studied by the procedures conventionally used for ceramics: lineal shrinkage, density ρ , open porosity P , mechanical strength under compression σ_c , minimum d_{\min} and maximum d_{\max} pore sizes, and permeability to air K .

The parameters of the porous structure of the material were evaluated by means of gas-liquid porometry [6].

The ceramic samples were obtained by cold pressing pre-sintered powders. The values of the shrinkage under high-temperature kilning of samples with NZP structure are presented in Table 2.

Kilning samples made of materials obtained by solid-phase synthesis showed that defect-free samples can be obtained only for strontium-based zirconium phosphate. Barium- and calcium-based zirconium phosphates sinter with an increase of volume and fracture.

All zirconium phosphates (Ca, Sr, Ba) synthesized by melting in solar furnaces made it possible to obtain a final product in the form of a ceramic with NZP structure without samples cracking or fracturing.

In summary, the production of ceramics by the conventional sintering method does not pose any difficulties for NZP compounds obtained by melting in a solar furnace. No increase in size is observed, and the size decrease at temperature 1250 – 1550°C indicates compaction of the structure and the possibility of obtaining ceramics with the required properties. This method not only decreases the preliminary synthesis time considerably but it also yields more perfect crystallization of the hexagonal lattice, which completely

eliminates mechanical destruction of the samples during ceramic kilning.

Laboratory-technological studies on obtaining microfiltration ceramics by semidry pressing with a consumable additive (20 wt.% coke above 100%) were performed. The sintering temperature of the samples took account of the coke addition and was determined by the mechanical strength of the samples. The samples were heated at the rate 300 K/h with soaking at the maximum temperature for 3 h. The initial compositions and properties of the ceramics are presented in Table 3.

It follows from the data in Table 3 that the sintering temperature determines the porosity and strength of the structures.

The practical significance of the work is that it expands the assortment of ceramic materials based on solid solutions with a network structure and regulatable properties. The results obtained can be used to develop new ceramic filtering materials with a low linear thermal expansion coefficient and high thermal stability and new catalysts for different technological processes.

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